# Products, Rates, and Mechanism of the Gas-Phase Condensation of Phenoxy Radicals between 500–840 K

Izabela Wiater,[a][‡] Jan G. P. Born,[a] and Robert Louw*[a]

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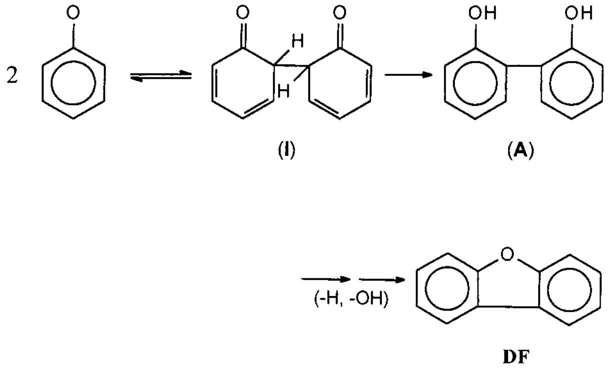
Phenols are demonstrated precursors of "dioxins" – polychlorinated dibenzo-*p*-dioxins (DDs) and dibenzofurans (DFs) – in thermal processes, especially incineration. Heterogeneous catalysis, depending on conditions, can play an important role, but mere gas-phase combination of phenolic entities to ultimately DD and/or DF is always possible. The present paper addresses the fundamental role of phenol itself. Phenol has long been known to give DF upon pyrolysis and in similar thermal reactions. In the liquid phase under oxidative conditions it yields five condensation products (**A**–**E**); this clearly occurs through the dimerization of two phenoxy (PhO) radicals, followed by enolisation/rearomatisation. Our study shows that in the gas phase, at the lower T end, such dimers are also formed, but still with very little DF. That DF, indeed, is almost the only condensation product at elevated temperatures is substantiated by thermochemical–kinetic analysis (favouring the pathway of *ortho*-C/*ortho*-C combination of two PhO radicals), as well as by results obtained with two plausible intermediates, viz. 2,2′-dihydroxybiphenyl (**A**) and 2-phenoxyphenol (**C**). Mechanisms for the requisite enolisation and dehydration steps leading to DF are discussed.

## Introduction

Thermolytic reactions of phenol have been investigated for a long time and are still actively researched for, for example, a better understanding of combustion mechanisms.

When subjected to heat, phenol yields dibenzofuran (DF). A German patent from the beginning of the 20th century, for example, outlines that phenol vapour, diluted with steam, mixed with air, and heated with or without contact substances resulted in dibenzofuran formation.[1] In another early example, dibenzofuran is also produced upon distillation of phenol over various substances, such as lead oxide.[1] DF formation in the homogeneous gas-phase pyrolysis and slow combustion of phenol has been ascribed to the dimerisation of two phenoxy radicals as the first step.[2,3] More recent kinetic and product studies[4,5] showed that DF formation from two phenoxy radicals can occur with an overall rate constant of $10^8$ $\text{M}^{-1}$ $\text{s}^{-1}$ and above, not so much less than $k$ for the first step, which is approximately $10^{10}$ $\text{M}^{-1}$ $\text{s}^{-1}$. A simple rationale is given in Scheme 1.[3,6]

While dimer **I** will revert to phenoxy radicals at elevated temperatures, enolisation to **A** (2,2'-dihydroxybiphenyl) can ultimately lead the way to DF. **A** has been found in trace amounts (next to DF) in the pyrolysis of phenol[4] and from the hydrogenolysis of anisole.[5] Also, at 500 °C authentic **A** can be rapidly converted into DF with high yield,[3] presumably by a radical (chain) process. The formation of dibenzo-*p*-dioxin (DD) was mentioned in none of these cases; significant proportions of (chlorinated) DDs arise, however, when *ortho*-chlorine substituents are introduced.[3,4,6,7]



Scheme 1. Formation of dibenzofuran through the dimerisation of phenoxy radicals

At higher temperatures, phenoxy radicals decompose unimolecularly into carbon monoxide and a cyclopentadienyl radical[8] (Equation 1):

$$C_6H_5O^\bullet \rightarrow c\text{-}C_5H_5^\bullet + CO \qquad (1)$$

This important reaction limits lifetimes – and concentrations – of phenoxy-type radicals, and hence their significance in "dioxin" (DF, DD) formation in incinerators.[9]

The phenoxy radical is resonance stabilized by 16 kcal/mol;[10] the electron spin is delocalized from oxygen to *ortho*- and *para*-C, and the C–O bond is shortened.[11,12] According to FMO theory, coupling of radicals occurs preferentially at the sites of the highest spin density. SOMO electron-spin densities calculated by AM1/UHF show the highest value for the *para* position,[13] but *ortho–ortho, ortho–para*, and *para–para* C–C coupling are all feasible. Coupling can also involve the oxygen, to give O–*ortho*-C, O–*para*-C dimers. The probability for the formation of the O–O dimer is low and, more importantly, it will be unstable even at ambient temperature. Methyl radicals gave cresols in more than 90% (expectedly via the methylcyclo-

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[a] Center for Chemistry and the Environment, Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University,
POB 9502, NL-2300 RA Leiden, The Netherlands
E-mail: R.Louw@chem.leidenuniv.nl

[‡] On leave (through TEMPUS grant IMG-97-Pl-2135) from Jagiellonian University, Faculty of Chemistry, Kraków, Poland

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hexadienones) and gave less than 10% anisole.[14] The *ortho*-/*para* ratio of cresol is 1.2–1.5, essentially independent of temperature. Armstrong et al.[15] investigated the products of the phenoxy + phenoxy combination upon the decomposition of di-*tert*-butyl peroxide (dTBP) in neat phenol at 140 °C over 24 h, and found all possible (enolised) condensation products; they are, in decreasing order: **A** > **B** > **C** ≈ **D** > **E** (Figure 1).

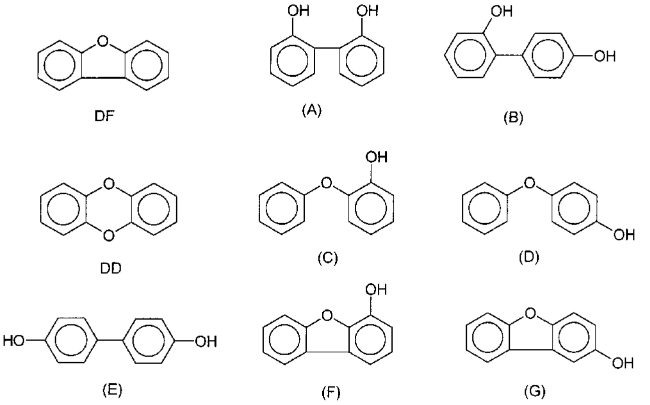


Figure 1. Structure of compounds; DF = dibenzofuran, DD = dibenzo-*p*-dioxin, A = 2,2'-dihydroxybiphenyl, B = 2,4'-dihydroxybiphenyl, C = 2-phenoxyphenol, D = 4-phenoxyphenol, E = 4,4'-dihydroxybiphenyl, F = 4-dibenzofuranol, and G = 2-dibenzofuranol

Born repeated this experiment, and found analogous results.[4] Interestingly, in a comparable gas-phase flow experiment at 340 °C, he found only **A** (major), **C**, and **D** with little DF (5% based on **A**).

Phenolic compounds and the corresponding phenoxy radicals play an important role in many biological and chemical processes. Lipids and other natural organic materials are protected from oxidative degradation by phenols.[16] The antioxidant action of sterically hindered phenols is widely used to protect synthetic materials. Phenols can break (aut)oxidation chains by H-donation to, e.g., chain-carrying peroxyl radicals; the hindered, resonance-stabilised aryloxyl radical is in most systems too unreactive to continue the chain; they rather dimerise. In model oxidation studies of phenols with available unsubstituted *ortho* or *para* positions, dihydroxybiphenyl derivatives are formed.[17] If all *ortho* and *para* positions are substituted (so that tautomerisation to the biphenyl skeleton is impossible) dimerisation can still take place; the type of the product depends on structure and experimental conditions.[18] If both *ortho* positions are occupied and the *para* position is free, *p*-diphenoquinones can be isolated. These arise from the *para* C–C coupled bisketo compound, through enolisation to the 4,4'-dihydroxybiphenyl and further oxidation.[18b] Oxidative coupling of phenols, via phenoxy radicals, is also of importance in biomimetic synthesis.[19] These examples of liquid-phase (aut)oxidation amply demonstrate the capacity of phenoxy-type radicals to dimerize. It also implicitly means that these radicals are quite unreactive towards (air) oxygen.[20]

Detailed insight into the thermal conversion of phenol/phenoxy is a prerequisite for understanding the behaviour of (poly)chlorinated analogues. The latter are demonstrated precursors of the notorious family of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), (often toxic) by-products of the combustion and other thermal processes involving chlorine-containing materials.[21]

This paper addresses the chlorine-free basic system: phenol. With quartz flow reactors, dilute vapours of phenol were induced to form phenoxy radicals, and their fate was monitored with emphasis on condensation products. At temperatures from 500 K, free radical initiators, e.g., *tert*-butyl hydroperoxide, served to form phenoxy in inert ($N_2$) atmospheres; at higher temperature (773 K), slow combustion – with substantial degrees of conversion of phenol – was also studied, the oxygen now enabling the generation of phenoxy radical intermediates.

## Results

The reactivity of phenoxy radicals was studied in flow reactors at 1 bar between 500–850 K, with emphasis on the higher temperature range (above 700 K).

Three types of experiments were performed:

(1) Peroxide-initiated pyrolysis of phenol, between 500–613 K, with residence times around 12 s.

(2) Nitromethane-initiated pyrolysis of phenol between 713 and 833 K, with residence times of ca. 8 s.

(3) Slow combustion of phenol together with an excess of benzene at 773 K, with a residence time of approximately 45 s.

Data of representative examples of experiments 1, 2, and 3 are collected in Table 1.

As seen in Table 1, the main product of phenoxyl combination in series 2 was dibenzofuran, with somewhat higher output levels at the lower end of the temperature range. As minor products, 2- and 4-phenoxyphenol (**C** and **D**), and 2,2'-dihydroxybiphenyl (**A**) were also observed. The compounds 2,4'- and 4,4'-dihydroxybiphenyl were not found (detection limit $10^{-4}$, calculated on PhOH). The results differ markedly from those of series 1, where DF was close to the detection limit, and **A** is the most abundant "dimer" found. The exit gases of series 1 and 2 contained CO, $C_2H_6$, and also some $C_2H_4$ in series 2, as degradation products of dTBP. As expected, the products of methyl–phenoxy combination were also formed. The most abundant was *o*-cresol, from 45% in experiment 2.2 to 54% in experiment 1.1; anisole was the least abundant product, from 8.7% in experiment 1.1 to 17% in experiment 2.3.
Experiments 3.1 and 3.2 exemplify the slow combustion of phenol diluted in benzene (1:30). Benzene was chosen as a diluent, because it is expected to be very stable under those conditions and, when reacting, to give similar products to

Table 1. Gas-phase conversions of phenol: dimeric products

| Exp.no | Temp. [K] | Ratio of "dimers" output[a] DF | A | C | D | | Sum, yield [2 × (mol/mol PhOH in)] |
|---|---|---|---|---|---|---|---|
| 1.1[b] | 503 | ND | 1 | 2 | 1 | | 0.0010 |
| 1.2 | 543 | 0.009 | 1 | 0.5 | 0.25 | | 0.0010 |
| 1.3 | 573 | 0.011 | 1 | 0.33 | 0.15 | | 0.0012 |
| 1.4 | 613 | 0.05 | 1 | 0.37 | 0.10 | | 0.0010 |
| 2.1[c] | 713 | 20 | 1 | 0.4 | 0.25 | | 0.0072 |
| 2.2 | 753 | 27 | 1 | 0.4 | 0.30 | | 0.0063 |
| 2.3 | 773 | 20 | 1 | 0.45 | 0.41 | | 0.0030 |
| 2.4 | 793 | 16 | 1 | 0.40 | 0.50 | | 0.0028 |
| 2.5 | 833 | 22 | 1 | 0.33 | 0.15 | | 0.0032 |
| | | DF | **A** | **C** | **G** | **F** | |
| 3.1[d] | 773 | 5 | 1 | 1.04 | 2.12 | 1.04 | 0.01 |
| 3.2 | 773 | 51 | 1 | 1.98 | 1.95 | 1.04 | 0.01 |
| 3a[e] | 773 | DF, see text | | | | | |
| 3b[e] | 843 | DF, see text | | | | | |

[a] **A**, **C**, **D**, **F**, **G**, DF – see Figure 1; ND = below detection limit. – [b] Series 1: Inputs (mol fraction): PhOH 0.02; *tert*-butyl hydroperoxide (TBHP) from 0.004 in experiment 1.1 to 0.002 (exp. 1.4); dTBP: 10 mol-% on TBHP, carrier gas $N_2$. Outputs of PhOH ≥ 90%, TBHP conversion ca. 85% in exp. 1.1 to complete (other exp's); di-*tert*-butyl peroxide (dTBP) conversion ca. 20% in exp. 1.1, ca. 40% in exp. 1.2, ca. 90% (exp. 1.3), to completion in exp. 1.4. Other salient products: ethane; anisole/*o*-cresol/*p*-cresol with ratio 10:53:37, 2–3%, based on PhOH. – [c] Series 2: Inputs (mol fraction): PhOH 0.0042; $MeNO_2$ 0.0035; filler gas $N_2$. Outputs of PhOH ≥ 90% except exp. 2.4: 80%; conversion of $MeNO_2$ < 10% (exp. 2.1), ca. 20% (exp. 2.2), 65% (exp. 2.3), 96% (exp. 2.4). Other salient products include ethane, anisole, cresols, as above. For further details, see ref. [4] [d] Series 3: Inputs (mol fraction): PhOH 0.00165 (exp. 3.1 ), 0.0014 (exp. 3.2); benzene 0.050; filler gas $O_2$ and $N_2$ (19:81). Outputs of PhOH ≥ 55%. – [e] Series 3a: Inputs (mol fraction): benzene 0.05; filler gas $O_2$ and $N_2$ (19:81).

that of phenol. For comparison, the slow combustion of benzene only (exp. 3a), under the same conditions, was also conducted. The "major" product of this blank run was phenol, around 0.01%, based on the input of benzene. The only other detectable product was DF (about 1% based on phenol, which is only ca. 0.8% of the DF obtained in exp. 3.1 and exp. 3.2).

In experiments 3 the conversion of phenol was approximately 40%. The main product was again DF, with a yield of 1–2% based on converted phenol. Further products found were **A**, **C**, **D**, 4-dibenzofuranol (**F**), and 2-dibenzofuranol (**G**), but in amounts nearly two orders of magnitude less than DF. After concentration of the obtained sample, a large number of other products, at trace levels (3–4 orders of magnitude below DF), could also be identified. These include DD, 2,4'-dihydroxybiphenyl (**B**), isomers of benzobisbenzofuran, phenoxyphenoxyphenol, and also methylated derivatives of **A**. The gaseous products were CO, $CO_2$, $CH_4$, and $C_2H_2$.

To better understand the chemistry of the condensation of phenoxy radicals, two possible intermediate products on the way to DF, namely 2,2'-dihydroxybiphenyl (**A**) and 2-phenoxyphenol (**C**), were chosen and their reactivity was examined.

When dilute vapours of **A** are subjected to thermolysis (in $N_2$ atmosphere) or to slow combustion at 773 K with residence times of around 100 s, conversion is quantitative, with high yields of DF (80 and 55%, respectively).[3] Once it was known that **A** is a precursor of DF, the slow combustion of **A** in a large excess of benzene (1:200) was conducted, as a step towards more realistic conditions. Under the conditions of experiments 3, the conversion of **A** was 99.93% and the only important organic products were phenol and DF; other products with two benzene rings, if present, comprise less than 1% on DF. Compared with the output of experiment 3a (benzene only), the output of phenol was six times higher. The selectivities from **A** to phenol and DF were 20–25% each. The latter output is less than half of that from neat **A**, but still quite significant.

The thermolysis of **A** in the lower temperature range (560–600 K), initiated by TBHP, was also studied briefly. Diluted in benzene (1:50) with about 1% peroxide on benzene, and with residence times around 90 s, ca. 20% of **A** is converted at 560 K and ca. 80% is converted at 600 K. The selectivity to DF is low, in the 1–2% range only. The formation of products such as biphenyl (from benzene) and the mono- and dimethyl ethers of **A** and of methylated cresol, as well as derivatives such as 2,2'-dihydroxy-5-methylbiphenyl, at least partially explain this. The oxyradical which can arise from **A** will be relatively long-lived at these mild temperatures, so it can undergo bimolecular reactions with other radicals, e.g., $\cdot CH_3$.

Slow combustion was focused on again, and several experiments with 2-phenoxyphenol (**C**) diluted in benzene, 1:220–600, were conducted at 773 K. Conversion of **C** was about 95% throughout. Remarkably, the major product next to phenol (about 10% on **C** input) was 4-dibenzofuranol (**F**) (about 4%). Two more products were detectable, viz. DF and DD, with reproducible yields of 14 and 9% on **F**, respectively. Based on the slow combustion of benzene only (exp. 3a), it turns out that about 25% of phenol and less than 10% of the DF can have been produced from benzene.

## Discussion

### (a) Radical-Induced Lower-Temperature Approaches

Both TBHP and nitromethane generate methyl radicals which will abstract hydrogen from phenol to form phenoxy radicals (Equation 2). Judging from recent data reported by Pedulli et. al.,[39] $k_2$ should be around $10^6$ $\mathrm{M}^{-1}$ $\mathrm{s}^{-1}$ at 600 K. This can be followed by combination of phenoxy with methyl radicals to give anisole, plus *o*-/*p*-cresols, the latter two compounds after tautomerisation of the respective keto forms (Equation 3).[14]

$$CH_3^{\bullet} + C_6H_5OH \rightarrow CH_4 + C_6H_5O^{\bullet} \tag{2}$$

$$CH_3^{\bullet} + C_6H_5O^{\bullet} \rightarrow C_6H_5OCH_3 + o\text{-}CH_3C_6H_4OH + p\text{-}CH_3C_6H_4OH \tag{3}$$

The site selectivities of O/*o*-C/*p*-C are ca. 10:55:35 in the peroxide series, and ca. 15:45:40 in the runs with $MeNO_2$; these results tally with those of Mulcahy and do not deviate much from what expected on the basis of spin-density data.[13] The strengths of the bonds made, 65 kcal/mol for O–C in anisole, and similar strengths in the keto-cresols (vide infra),[22] ensure that the $\cdot CH_3$ additions to $PhO^{\bullet}$ are irreversible in the temperature range studied. Therefore, tautomerisation to the "real" cresols is the most likely fate of the latter. A simple intramolecular H-shift will be rather slow due to orbital-symmetry restrictions,[23] but polar molecules and/or surfaces can be of great help here. We will come back to this aspect in section (c).

Analogously to methyl–phenoxy recombination, phenoxy radicals can recombine through C–O coupling (requiring one following keto–enol tautomerisation) and by C–C-bonding at the *ortho* and/or *para* positions (needing two rearrangements).

$$2\,C_6H_5O^{\bullet} \rightarrow 2\text{-}C_6H_5OC_6H_4OH\ (\mathbf{C}) \tag{4}$$

$$2\,C_6H_5O^{\bullet} \rightarrow 4\text{-}C_6H_5OC_6H_4OH\ (\mathbf{D}) \tag{5}$$

$$2\,C_6H_5O^{\bullet} \rightarrow 2{,}2'\text{-}HOC_6H_4\text{–}C_6H_4OH\ (\mathbf{A}) \tag{6}$$

$$2\,C_6H_5O^{\bullet} \rightarrow 2{,}4'\text{-}HOC_6H_4\text{–}C_6H_4OH\ (\mathbf{B}) \tag{7}$$

$$2\,C_6H_5O^{\bullet} \rightarrow 4{,}4'\text{-}HOC_6H_4\text{–}C_6H_4OH\ (\mathbf{E}) \tag{8}$$

Dimerisation to give $C_6H_5O\text{–}OC_6H_5$ will be highly reversible due to its very weak peroxide bond which, due to the resonance energy in $C_6H_5O^{\bullet}$, will be ca. 15 kcal/mol only.

In both series 1 and 2 only three of the five possible products have been positively identified: **A**, **C**, and **D**; the *p*-C/*p*-C and *o*-C/*p*-C condensation products, if present, were below 1% based on **A**. This contrasts with the results of Armstrong et al.[15] on the peroxide-initiated liquid-phase reaction (140 °C), wherein the overall site selectivities centred around O/*o*-C/*p*-C ≈ 10:60:30. This points at reversibility in the gas phase, at least with respect to the *p*-site in phenoxy. Thermokinetic aspects are discussed in section (c); it will suffice here to point out that bonds between two PhO radicals are much weaker than those between PhO and methyl.

At $T < 600$ K, series 1, outputs of DF are very minimal, but in series 2, ($T > 700$ K) it is the major product. If **A** is accepted to be the intermediate, its conversion into DF is probably facilitated by $NO_2$; H-abstraction from ArO–H by $NO_2$ will be mildly endothermic (ca. 10 kcal/mol), but with $(NO_2) > 10^{-5}$ M; the half-life of ArOH in this process will be less than 0.1 s.

### (b) Slow-Combustion Series

Combustion reactions are mostly of a radical-chain nature.[24] In the slow combustion of phenol, when free-radical initiators are not deliberately used, measurable reaction occurs above 700 K. $O_2$, a triplet biradical, may abstract H from phenol (Equation 9), but this reaction – endothermic by ca. 40 kcal/mol, will be several orders of magnitude too slow to account for observed degrees of reaction. Without detailing the mechanism here, radical species (e.g., $HO_2^{\bullet}$ and, more importantly, $^{\bullet}OH$ at higher $T$, Equation 10) will be instrumental in the (depending on conditions, reversible) formation of phenoxy radicals.[24,25]

$$PhOH + O_2 \rightarrow PhO^{\bullet} + HO_2^{\bullet} \tag{9}$$

$$PhOH + Z^{\bullet} \rightarrow PhO^{\bullet} + ZH\ (Z = HO_2^{\bullet}, {}^{\bullet}OH, {}^{\bullet}O^{\bullet}) \tag{10}$$

Phenoxy radicals can recombine as described in section (a) or can undergo decomposition.[8]

Product patterns and levels strongly depend on temperature. So the reaction of benzene/PhOH (20:1) at 843 K led to larger outputs of phenol (due to its substantial formation from benzene at this temperature), high levels of CO and $CO_2$ and concomitant higher outputs of DF. Also, some products not seen in experiment 3a, such as benzonaphthofuran, are detected.

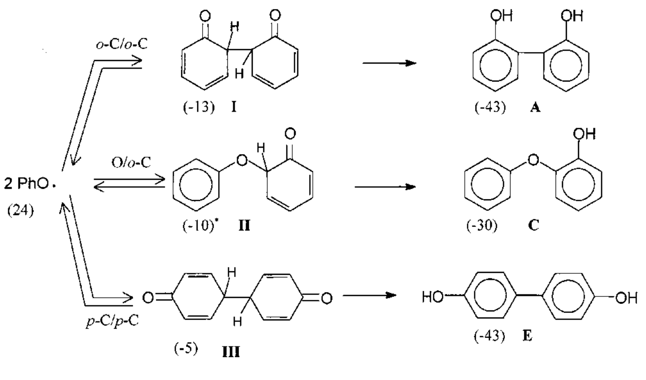
In experiments 3 at 773 K, about one-half of phenol is smoothly converted, and by far the major condensation product is again DF. Only a few percent (based on DF) of **A** and **B** are formed, and products involving the *para* site of phenoxy (e.g., **D**) are even much less abundant. Relatively important are **F** and **G**, hydroxy derivatives of DF. Given the extremely low yield of phenol upon slow combustion of benzene (exp. 3a), **F** and **G** have not been formed by secondary oxidation of DF, but rather via some other "dimer" precursors. In the formation of DF, *o*-C/*o*-C combination is an important (but not necessarily the only) product channel, as the results of slow combustion with added **A** demonstrate. We will discuss other possible pathways to/via dimers of phenoxy in more detail after the discussion of the thermochemical–kinetic analysis of section (c). Here we will briefly comment on the results of the "blank" slow combustion of benzene only.

At 773 K, benzene is still almost inert. Traces of phenol and DF (ratio 100:1) are the only aromatic products seen. After evaporating nearly all of the benzene from the product, the MS analysis begins to show "noise" from ultratrace compounds, which may also stem from contaminants in the benzene. To get more meaningful results, the temperature must be well above 773 K. In the slow combustion of benzene at 843 K (exp. 3b), yields of phenol and DF are increased (PhOH 2% on benzene input, DF 1.5% on PhOH). Some other products are seen by GC-MS, especially after sample concentration: Biphenyl ≈ 50% on DF; also traces of other PAH, for example, naphthalene, etc.; **C** and **D** each are present in a few percent, based on DF. Furthermore, some methylated derivatives of biphenyl and DF, as well as **B** and benzobisbenzofuran, each with yields two to three orders of magnitude less than DF; finally traces of DD, three to four orders of magnitude less than DF, were detected. The product pattern is not unlike that of the slow combustion of phenol/benzene, but the levels are much lower.

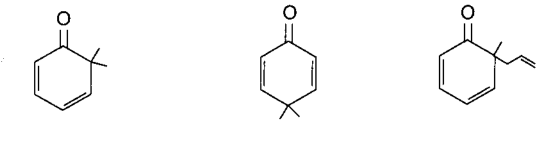
### (c) Thermochemical–Kinetic Aspects

In slow combustion and thermolysis at elevated temperature (> 700 K), net rates of formation of DF, the major condensation product from two PhO$^{\bullet}$ radicals imply rate constants of $10^{8}$–$10^{8.5}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[5,6] This also means substantial reversibility (if not equilibration) in the process: 2 PhO ⇄ dimers, as the forward rate constant will be close to $10^{10}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[26] Then, site selectivities for combination will lose relevance at the expense of (differences in) bond strengths, combined with rates for consecutive reactions, e.g. tautomerization.

We will now discuss this for three of the five possible PhO/PhO dimerizations, taking into account the best available thermochemical data; see Scheme 2.[10] Standard gas-phase heats of formation of **A**, **C**, and **E** have, to our knowledge, not been directly measured, but can be approximated well, by starting from biphenyl (43.5 kcal/mol) and diphenyl ether (12.5 kcal/mol),[27] and by employing the increment benzene → phenol of –43.[28] To arrive at the enthalpies of **I** and **III**, twice the heats of "ketonisation" must be added. Accepting that **V** is 4 kcal less stable than **IV**[10] (see Figure 2), we place the absolute value for **IV** at –8 kcal/mol,[29] on various grounds, so 15 kcal/mol endothermic, compared to phenol. Applying the respective increments to **I** and **III** leads to the bracketed values in Scheme 2. The enthalpy of **II** is based on that of **IV**, since replacement of an H at ($sp^3$) carbon, R–H → R–OPh, R = e.g., Me or Et, has almost no change on the enthalpy of formation. From Scheme 2 the enthalpy diagram of Figure 3 is obtained, which can serve to rationalise rates and products, also as a function of temperature.



Scheme 2. Pathways for the condensation of phenoxy radicals



(-8) **IV** (-4) **V** **VI**

Figure 2. Structures of compounds **IV**, **V**, and **VI**

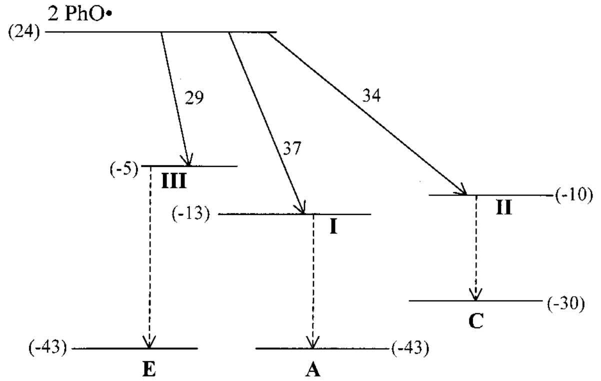


Figure 3. Enthalpy diagram (cf. Scheme 2)

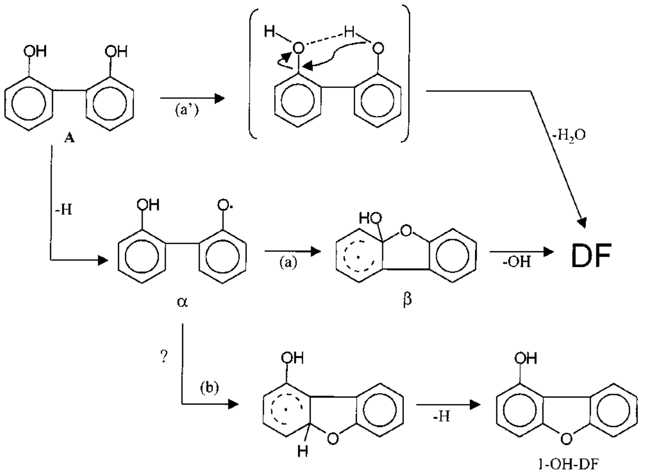
At lower temperatures, say up to 400 K, any of the five possible combinations can be formed, obeying the kinetic site selectivities in the phenoxy radical, and the dimers will tautomerize to the final aromatic products, certainly in the liquid phase. With increasing temperature, in the vapour phase, redissociation comes into play, first for **III**, and last for **I**. If we accept an Arrhenius $\log A/\mathrm{s}^{-1}$ value of 15 throughout, calculated half-lives at 700 K will be ca. 0.02 s (for **I**), 0.002 s for **II**, and ca. 1 µs for **III**. At 800 K, the $k$ value for dissociation of **I** is ca. $10^{5}$ $\mathrm{s}^{-1}$, that for **III** is two orders of magnitude larger. Recalling that, in slow combustion, the (net) rate of condensation of two PhO$^{\bullet}$ groups to DF is $10^{8+}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$, up to two powers of ten below $k$ for radical/radical combination, formation of **I**–**III** (and the other two isomers, from O/*p*-C and *o*-C/*o*-C coupling) must be reversible. Then, **I** will greatly predominate. In order to go to the final product(s) – taking 800 K as a reference again – the (pseudo-first-order) rate constant to describe the consecutive enolisation, **I** → **A**, has to be $10^{3}$–$10^{4}$ $\mathrm{s}^{-1}$ to satisfy the thermokinetic model. (At the same time, this rate constant should not be so very much larger. When $10^{6}$ $\mathrm{s}^{-1}$ is exceeded, combination of two PhO$^{\bullet}$ groups will no longer be reversible, and overall rates (to DF) would approach the radical/radical encounter rate limit).

Direct 1,3-H shifts from C to O will be (too) slow, being "forbidden" due to orbital symmetry mismatch.[23] Neither this, nor "substitution of hydrogen" by some unprecedented simultaneous H shift, as very recently advanced by Hagenmaier[31] can be considered as a satisfactory mechanistic interpretation. A clue to this is the behaviour of allyl phenyl ether upon (attempted) gas-phase Claisen rearrangement.[32] This reaction *does not occur in dry, inert environments* (this implies that the first step to **VI** is endothermic, which puts a lower limit to its heat of enolisation[29]). With proper (e.g., hydroxylic) agents the overall Claisen two-step reaction to *o*-allylphenol proceeds with rates consistent with extrapolated liquid-phase data. These phenomena can also be explained by enolisation rates such as those mentioned above.[33]

### (d) The Fate of Intermediates

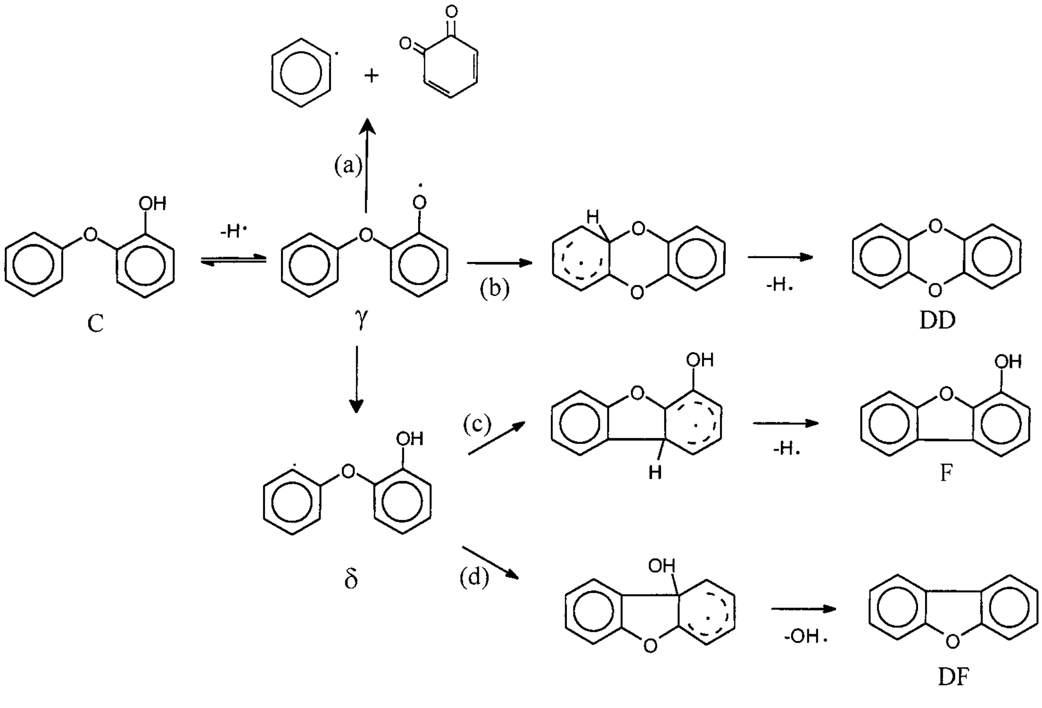
In slow combustion, 2-phenoxyphenol (**C**) is much less stable than phenol itself (95 vs 45% conversion at 773 K, respectively). While formation of the 2-phenoxyphenoxy radical may be easier due to a somewhat lower O–H bond strength, the increased reactivity of this radical is in our view more important. One possibility is fragmentation, (a) in Scheme 3; the *o*-quinone will be rapidly degraded, and phenyl radicals can in part form phenol, via phenoxy radicals formed upon reaction with $O_2$.[34,35] The intramolecular reactions (b), (c), and (d) in Scheme 3, adequately explain the formation of **F**, the most prominent product, DF and DD.[36]

The slow combustion of 2,2'-dihydroxybiphenyl (**A**) gives essentially only one condensation product, DF, in large yields. Here, splitting of the corresponding aryloxy radical is not possible. The overall dehydration **A** → DF can be rationalized again in terms of free radical steps [Scheme 4, (a)], but it is not immediately clear why the alternative (b) with about the same thermokinetic characteristics, does not seem to occur. (The expected product, 1-hydroxydibenzofuran, could not be detected; if present it must be below 0.1% based on DF). The overall high rate of conversion **A** → DF suggests that the loss of $H_2O$ may occur at least in part by nonradical reactions (at the wall, or promoted by $H_2O$), schematically depicted as an intramolecular reaction (a').

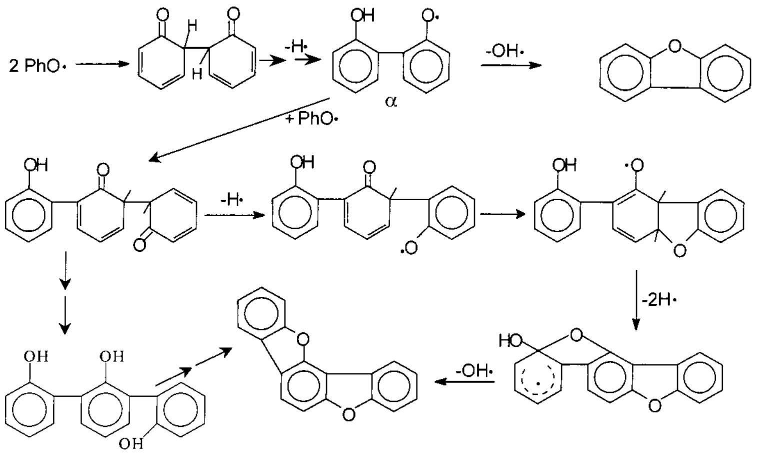


Scheme 4. Slow combustion of 2,2'-dihydroxybiphenyl (**A**)

In addition to DF and the other, intermediate, products built from two phenoxy entities as discussed before, several "tricyclic" condensation products were detected by GC-MS, in particular, (isomers of) benzobisbenzofuran and of phenoxy-phenoxyphenol. The simplest rationale is by condensation of phenoxy with a higher homologue, such as α (Scheme 4) or γ (Scheme 3). These combination reactions can indeed be competitive with unimolecular steps of, e.g., α to DF, due to the substantial barriers of around 35 kcal/mol for such reactions.[36] Scheme 5 illustrates how radical α can condense with phenoxy, by *o*-C/*o*-C coupling, either by radical or nonradical pathways, to (one isomer of) benzobisbenzofuran. Whether or not still higher condens-



Scheme 3. Conversion of 2-phenoxyphenol (**C**)



Scheme 5. Rationale for the formation of benzobisbenzofuran

ates were formed is unknown, as these products were not volatile enough to be seen by our GC-MS analysis.

In summary, we conclude that in the gas phase at moderately elevated temperatures, up to approximately 850 K, phenoxy radicals condense to yield dibenzofuran, DF, with only (very) small proportions of other products of similar complexity, including dibenzo-*p*-dioxin, DD. This may be understood on the basis of thermochemical kinetics, if the best available consistent data is used; this indeed favours the product channel by *o*-C/*o*-C coupling with subsequent tautomerization and, overall, dehydration steps.

## Experimental Section

**Purity of Chemicals:** Tank $N_2$ 99.99% and $O_2$ 99.99% were supplied by Hoekloos in standard cylinders. 20% Di-*tert*-butyl peroxide in 80% *tert*-butyl hydroperoxide (Fluka, pure), nitromethane (Janssen, 96%) were used without further purification, except for the experiments with 2,2'-dihydroxybiphenyl, for which the *tert*-butyl hydroperoxide was distilled prior to use. Phenol (Merck, pro analysis), benzene (Merck, for spectroscopy, distilled), toluene (J. T. Baker, >99.5%), 2,2'-dihydroxybiphenyl (Janssen Chimica, 99%) were checked by GC to be of adequate (>99%) purity and were used as such. For 2-phenoxyphenol synthesis: 2-bromophenol (Janssen Chimica, 98%), KOH (Boom B.V Meppel, 85%), diethyl ether (J. T. Baker, >99.5%), petroleum ether 60–80 (Baker, pure) were used without further purification. Reference compounds: bromobenzene, dibenzofuran, dibenzo-*p*-dioxin, 2-dibenzofuranol, and 4-dibenzofuranol were all high-grade (>99%) products.

**General:** All experiments were conducted in quartz cylindrical flow reactors of 6.2 mL (length 47 mm, 13 mm ID) for series 1 and 2, and of 340 mL for experiments 3; these reactors were placed either horizontally or vertically in an electrically heated oven. The temperature was controlled by a proportional regulator and was monitored with chromel-alumel thermocouples displayed on digital thermometers (Therma 1, type ST-861-107). The upper and lower ends of the oven were insulated by quartz wool. For further details on these set-ups see Refs.[4,6]

In experiments 1 and 2, substrates were continuously fed into the reactor by evaporation of the liquid. For this a constant inflow of $N_2$, regulated with mass-flow controllers, was passed through an impinger filled with the liquid substrate. For phenol itself, an oil-operated thermostatic bath was used to maintain the molten compound at a fixed temperature (74 °C) in a stainless steel impinger; a stable vapour pressure at the required level was thus created. The mixture of dTBP and TBHP (initially 20:80) was kept in a Pyrex evaporator at 20 °C and was added to the phenol by passing through a calibrated stream of $N_2$. Nitromethane was evaporated from a stainless steel impinger kept at 20 °C by a water-run thermostatic bath.

In experiment 3, gas flows of $N_2$ and $O_2$ were regulated with needle valves and were measured with capillary flow-meters. Liquid reactants were introduced by means of a calibrated motorised syringe pump (B.Braun Melsungen, Perfusor VI type 871222/0) through a gas-tight rubber septum, and they were vaporised into the gas flow before they entered the reactor.

The entrance and exit tubes of the reactors were heated to over 200 °C by wrapped heating tapes to prevent condensation of the less volatile organic substances.

For series 1 and 2, an on-line set-up was used. A two-way switching valve led the gas mixture either directly or via the reactor towards the on-line gas chromatograph for analysis before or after reaction. The exit gas, after mixing with methane (internal standard) was also analysed on-line by GC-FID with a packed carbowax (2 m × 1/8" ID) column and a methaniser.[4]

In experiment 3, condensable products were collected in a cold trap. The trap, containing toluene with an internal standard (bromobenzene), was cooled by acetone with liquid nitrogen. Exit noncondensable gases were analysed with a Packard series 428 GC equipped with an FID detector, Carboplot 007 column and a methaniser, calibrated by independent injections of a standard gas mixture.

Products in the toluene catch were quantified with a Hewlett Packard 5890A gas chromatograph with FID with a CP-SIL5-CB column (50 m × 0.32 mm ID), operated by HP Chem Stations. Toluene solutions (2 μL portions) were injected by an autosampler (Hewlett Packard 6890 Series) at a split ratio of 1:15. Absolute concentrations were deduced from the peak areas, after calibration by injecting standard mixtures of known composition. A Hewlett Packard 5890 GC-MS was used to identify unknown products.

Some samples were concentrated by solvent evaporation with a gentle stream of $N_2$, to allow better measurement of trace products.

**Synthesis of 2-Phenoxyphenol:** 2-Phenoxyphenol was prepared according to the procedure described in ref.[38] A comparable amount of DD was formed. The product mixture was liquefied in toluene, treated with 10% KOH and extracted with water. This extract was acidified with diluted HCl, extracted with toluene and checked by GC-MS. Toluene was gently evaporated with a stream of $N_2$. The crystalline product was dissolved in *n*-pentane and was kept at –20 °C for a few days for recrystallisation. The purity of the sample used in the slow combustion with benzene was checked by GC to be 99% (1% of DD).

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[28] This approach means that the C–OH bond strengths in **A** and **C** are taken to be identical to that in phenol. Likewise, $\Delta H^0_{f298}$ of hydroxy-biphenyl should be ca. 0 kcal/mol. Remarkably, the NIST compilation,[10] based on the original French paper,[37] advocates +8.5 for the *p*-isomer and 4 kcal/mol for *ortho*-hydroxybiphenyl. The idea that these C–OH bonds are much (4–8.5 kcal) weaker than in phenol and the idea that the *para* form should be no less than 4 kcal destabilized relative to *ortho* form must be in error.

[29] Ref.[10] advances that $\Delta H^0_{f298}$ (**IV**) = –17 ± 3 kcal/mol, so roughly only 6 kcal greater than that of phenol. As will be explained in more detail elsewhere,[30] this cannot be correct. One argument is that it would make **VI** about 5 kcal more stable than allyl phenyl ether, with the consequence that, contrary to observation,[32] the gas-phase Claisen rearrangement should also proceed in an inert environment (enolisation of **VI** occurring after cooling and condensing the reactant vapours). Another reason for rejecting this is that the value of –17 kcal/mol for **IV** is very much lower than that calculated from group additivity, from cyclohexadiene (25) and the increment for C=O replacing $–CH_2–$, i.e., –25, hence 0 kcal/mol; it is unrealistic to have an additional delocalization energy of more than 15 kcal/mol in this dienone system.

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[33] With $\Delta H^0_{f298}$ values of –1 kcal/mol for $PhO–CH_2–CH=CH_2$, and +7 kcal/mol for **VI**, and accepting rate parameters for the forward reaction: $\log A/s^{-1} = 11$, $E_a = 32$, those for the reversal of **VI** to starting compound will be $\log A \approx 11$ and $E = 24$ kcal/mol. At 800 K this means $k \approx 10^{4.4}$ $s^{-1}$. The vapour of added acetic acid could make the "rate constant" for competitive enolisation equal to or larger than this.

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[36] Without detailing the thermochemistry, reaction (a) is ca. 47 kcal endothermic, while the reactions by (b)–(d) are associated with activation barriers of some 35 kcal/mol. While scission (a) will have an Arrhenius *A* value of ca. $10^{15}$ $s^{-1}$, the other are intramolecular additions with much lower *A* values, e.g., $10^{10}$ $s^{-1}$. As a result, (a) can effectively compete with (b)–(d), the more so at higher temperatures.

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